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(54) Title: NUCLEAR FUEL REPROCESSING

(57) Abstract

There is described a method for treating or reprocessing spent nuclear fuel to substantially separate fissile material from fission products which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid and in particular to recover uranium and/or plutonium. There is also described a novel crystal structure.

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NUCLEAR FUEL REPROCESSING

The present invention relates to the treating or reprocessing of nuclear fuel using ionic liquids and to a novel form of a uranium compound.

Most commercial nuclear fuel reprocessing plants use the Purex process, in which the spent fuel is dissolved in nitric acid and the dissolved uranium and plutonium are subsequently extracted from the nitric acid solution into an organic phase of tributyl phosphate (TBP) dissolved in an inert hydrocarbon such as odourless kerosene. The organic phase is then subjected to solvent extraction techniques to partition the uranium from the plutonium. The Purex process involves a number of difficulties and is subject to continuous research and development activities to ameliorate these problems.

Internationally there are also two well developed processes which use molten salts for the reprocessing/waste conditioning of irradiated nuclear fuel. The Argonne National Laboratory electrometallurgical treatment process (ANL – EMT) and the Dimitrovgrad SSC – RIAR process both use molten salts at high temperatures (773 and 1000K, respectively). The ANL process is fundamentally electrorefining technology, using current flow to ensure the oxidation of a uranium anode to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as uranium metal. The SSC – RIAR process uses chemical oxidants (chlorine and oxygen gases) to react with powdered UO_2 fuel to form higher oxidation state compounds such as UO_2Cl_2 which are soluble in the molten salt. At the cathode the uranium compounds are reduced to UO_2 which forms a dendrite deposit.

Molten salts have been proposed for use in the reprocessing of irradiated fuels from Light Water Reactors (LWRs). These molten salts are typically mixtures of salts which are liquid only at high temperatures and this causes inherent disadvantages in a reprocessing plant.

Ionic liquids free of molecular solvents were first disclosed by Hurley and Wier in a series of US patents (24446331, 2446339, 2446350). These ionic liquids comprised

aluminium(III) chloride and a variety of N-alkylpyridium halides, and afforded a conducting bath for aluminium electroplating. In general terms an ionic liquid is a salt, a mixture of salts, or a mixture of components which produce a salt or salts, which melts below or just above room temperature (in terms of this invention, a salt consists entirely of cationic and anionic species). The term "ionic liquid" relates to a salt, a mixture of salts, or a mixture of components which produce a salt or salts, and which melts at a temperature up to 100°C eg from -50 to 100°C. The cation in these ionic liquids is usually organic.

Traditionally molten salts melt above 150°C, and more frequently at much higher temperatures than this. Such salts are usually composed of inorganic cations. and are only suitable for high temperature processes. There is therefore novelty in the application of ionic liquids to fuel reprocessing.

Known ionic liquids include aluminium(III) chloride in combination with an imidazolium halide, a pyridinium halide or a phosphonium halide. Examples of the halides include 1-ethyl-3-methylimidazolium chloride, *N*-butylpyridinium chloride and tetrabutylphosphonium chloride. An example of a known ionic liquid system is a mixture of 1-ethyl-3-methylimidazolium chloride and aluminium(III) chloride.

E. S. Lane, J. Chem. Soc. (1953), 1172-1175 describes the preparation of certain alkylpyridinium nitrate ionic liquids, including sec-butylpyridinium nitrate. No use of the liquids is mentioned but reference is made to the pharmacological activity of decamethylenebis(pyridinium nitrate).

L. Heerman et al., J. Electroanal. Chem., 193, 289 (1985) describe the dissolution of UO_3 in a system comprising *N*-butylpyridinium chloride and aluminium(III) chloride.

K. R. Seddon, J. Chem. Tech. Biotechnol. 1997, **68**, 351-356 discusses the design principles for room-temperature ionic liquids, some of their properties and the rationale for using these solvents.

International Patent Application WO 96/32729 teaches that oxide nuclear fuels may be dissolved in a fused alkali metal carbonate to produce a compound which may be further processed so as to extract uranium therefrom.

International Patent Applications WO 95/21871, WO 95/21872 and WO 95/21806 relate to ionic liquids and their use to catalyse hydrocarbon conversion reactions (e.g. polymerisation or oligomerisation of olefins) and alkylation reactions. The ionic liquids are preferably 1-(C_1-C_4 alkyl)-3-(C_6-C_{30} alkyl) imidazolium chlorides and especially 1-methyl-3-C_{10} alkyl-imidazolium chloride, or 1-hydrocarbylpyridinium halides, where the hydrocarbyl group is for example ethyl, butyl or other alkyl.

International Patent Application No PCT/GB97/02057 (WO 98/06106) describes a method of dissolving in an ionic liquid a metal in an initial oxidation state below its maximum oxidation state, wherein the ionic liquid reacts with the metal and oxidises it to a higher oxidation state. The initial metal may be in the form of a compound thereof and may be irradiated nuclear fuel comprising UO_2 and/or PuO_2 as well as fission products. Typically the ionic liquid is nitrate-based, for example a pyridinium or substituted imidazolium nitrate, and may contain a Brønsted or Franklin acid. Suitable acids are HNO_3, H_2SO_4 and [NO^+]. This International Patent application also describes certain novel ionic liquids, including 1-butylpyridinium nitrate, 1-octylpyridinium nitrate, other nitrate-based ionic liquids whose cation component is not exclusively alkylpyridinium or polymethylenebis (pyridinium), and substituted imidazolium nitrates, especially 1-butyl-3-methylimidazolium nitrate, 1-hexyl-3-methylimidazolium nitrate and 1-octyl-3-methylimidazolium nitrate.

Specifically, the oxidising ionic liquids described in WO 98/06106 may i) be intrinsically oxidising, ii) have an oxidising agent added, and/or iii) have a promoting agent of oxidising ability added. The agents may be an oxidant dissolved in a non-oxidising liquid or an auxiliary agent to increase the oxidising reactivity of another oxidising species. If the solvent contains nitrate ions, the agent increases the oxidising reactivity of the medium beyond that which would be provided by the nitrate ions themselves; as described above, such agents include acids and particularly Brønsted and Franklin acids.

[A Brønsted acid is a proton donor; conversely, a Brønsted base is a proton acceptor. A Franklin acid is a species which will give to a solvent a cation which is characteristic of the solvent system, e.g. $[NO]^+$ in the solvent N_2O_4; protons are not Franklin acids. A Lewis acid is any species which is an electron-pair acceptor. There are a wide range of species which can be described as Lewis acids, including BCl_3, H^+ or transition metal ions. A Lewis base is an electron-pair donor. A superacid is an acidic medium with a Hammet acidity function $-H_o$ which has a value above 6. Superacids are upward of 10^6 times as strong as a 1M aqueous solution of strong acid (ref. G. A. Olah. G.K.S. Prakash and J. Sommer, Superacids, Wiley, Chichester. 1985.)

The solvent may in principle comprise any ionic liquid but the liquid normally comprises nitrate anions.

The cation will in practice comprise one or more organic cations, especially nitrogen heterocycles containing quaternary nitrogen and more especially *N*-substituted pyridinium or *N,N'*-disubstituted imidazolium. The substituents are preferably hydrocarbyl and more preferably alkyl, which may be branched, for example. The hydrocarbyl (e.g. alkyl) groups usually contain from 1 to 18 carbon atoms and some usually from 1 to 8 carbon atoms.

The cation may therefore be a disubstituted imidazolium ion where the substituent groups take the form C_nH_{2n+1} for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups. In preferred disubstituted imidazolium ions one substituent has n=1, 2, 3 or 4 (of which methyl is particularly preferred) and the other has n=2, 3, 4, 5, 6, 7 or 8 (of which octyl, hexyl and more particularly C_4 especially butyl are preferred, linear groups are preferred). Alternately, the cation might be a substituted tetra-alkylammonium ion, where the alkyl groups take the form of C_nH_{2n+1} for $1 \geq n \leq 6$, and are linear or branched groups. A preferred example is tetrabutylammonium. However the alkyl groups might be of different lengths. Alternatively, the cation might be a substituted pyridinium ion, where the substituent group also takes the form C_nH_{2n+1} for $1 \leq n \leq 8$, and the substituent groups are linear or branched groups; suitable substituents include butyl, 2-(2-methyl)propyl, 2-butyl and octyl but straight chain alkyl, especially butyl, is preferred.

Of course, minor quantities of contaminants may be present, e.g. protonated – methylimidazole in 1-butyl-3-methylimidazolium.

The nitrate-based ionic liquids of WO 98/06106 may be prepared by mixing aqueous silver(I) nitrate together with an appropriate organic halide. By way of example, one such ionic liquid is prepared by mixing together solutions of aqueous silver(I) nitrate and 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Silver chloride is precipitated and the liquid 1-butyl-3-methylimidazolium nitrate is formed:

$$Ag[NO_3](aq) + [bmim]Cl(aq) \rightarrow AgCl(s) + [bmim][NO_3](aq)$$

The product may be purified by filtration and removing excess water from the filtrate.

1-hexyl-3-methylimidazolium nitrate is prepared by a similar method and this material is also a liquid at room temperature.

Alternative cations to pyridinium and imidazolium include quaternary phosphonium cations, e.g. tetrahydrocarbylphosphonium. Suitable hydrocarbyl groups are as described above in relation to pyridinium and imidazolium cations. Examples include unsymmetrically substituted phosphonium cations.

"The agent added to the ionic liquid to enable the oxidising process to occur more efficiently is typically an acid", notably a Brønsted acid (e.g. HNO_3 or H_2SO_4) or a Franklin acid, for example $[NO^+]$, serving in either case to make the medium more oxidisingly reactive towards substrates such as, for example, UO_2 or PuO_2. In other words, one class of oxidising ionic liquids contains an oxidant comprising nitrate and a promoter thereof. The agent when combined with the ionic liquid may react with the ionic liquid to create a new species which is also an ionic liquid. Thus, $[NO][BF_4]$ is believed to react with the nitrate salts of organic cations to form the tetrafluoroborate(III) salt of the cation. An exemplary reaction is:

$$[Bu\text{-}py][NO_3] + [NO][BF_4] \rightarrow N_2O_4 + [Bu\text{-}py][BF_4]$$

wherein Bu-py is 1-butylpyridinium, and $[Bu\text{-}py][BF_4]$ is an ionic liquid.

Whilst the methods and ionic liquids described in WO 98/06106 are suitable for general use and, in particular, use in nuclear fuel reprocessing, we have now found an advantageous method which is an improvement over the prior art. In particular, WO 98/06106 does not describe clear separation and/or product recovery steps.

According to the present invention we provide a method for treating or reprocessing spent nuclear fuel to substantially separate fissile material from other components of irradiated fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid. By the term substantially separate is meant partially separate, but preferably completely separate.

By the term other components of irradiated fuel, it is intended to include fission products, lanthanides, actinides and/or cladding materials. The method of the invention may preferentially also include the step of treating the ionic liquor, resulting from the step of dissolving spent nuclear fuel in an ionic liquid, by solvent extraction to separate the fissile material from other components of irradiated fuel.

The ionic liquid is preferably an oxidising ionic liquid as described in WO 98/06106, which is incorporated herein by reference, particularly one containing an acid, e.g. a Brønsted, Lewis, Franklin or superacid; although Brønsted and Franklin acids are preferred. Where an oxidising ionic liquid is used, the process involves oxidation of U(0) or U(IV) (normally as UO_2) to U(VI) and usually of Pu(IV) (normally as PuO_2) to Pu(VI); for example, uranium dioxide is oxidised to *trans*-dioxouranium(VI) in complexed form and plutonium dioxide to *trans*-dioxoplutonium(VI) in complexed form. Whatever the ionic liquid solvent, the dissolution of plutonium and uranium for recycling will normally involve the unavoidable dissolution of other components of the irradiated fuel. The reprocessing methods form a fissile material optionally in the form of an intermediate or final nuclear fuel product, e.g. a gel, a powder, a master batch material, a fuel pellet, a fuel

pin or a fuel assembly. The dissolution may involve dissolution of the cladding of a fuel rod, e.g. a stainless steel or magnesium alloy cladding or a zirconium alloy cladding such as that sold under the trade mark Zircaloy; after irradiation of fuel, Zircaloy cladding has a passivating oxide coating and dissolution of Zircaloy cladding therefore involves non-oxidative dissolution of oxidised Zircaloy (zirconium alloy). The dissolution of the Zircaloy may be oxidative or non-oxidative. As an alternative to chemical removal of the cladding, as for example by dissolution in an ionic liquid, it may be removed prior to the dissolution of the fuel in the ionic liquid, whether by mechanical or chemical means.

Accordingly, one class of methods comprises contacting zirconium alloy clad irradiated fuel with an ionic liquid to dissolve the cladding and the fuel. For use in dissolving cladding the ionic liquid preferably contains sulfate and may contain sulfuric acid, which has been found to react with the zirconium oxide layer on Zircaloy cladding. These methods may include immersing individual fuel pins or fuel assemblies in the ionic liquid within a suitable vessel.

A second class of methods includes the step of rupturing the cladding mechanically to expose the fuel pellets to the ionic liquid. In other methods, the fuel rod is placed initially in a first ionic liquid for dissolving the cladding and subsequently in a second ionic liquid for dissolving the uranium and plutonium or, optionally, compounds thereof. For dissolving fuel rods such as uranium or plutonium, a nitrate ionic liquid is preferred.

The dissolving of cladding may be carried out as a separate step to the dissolving of fuel, in which case different ionic liquids may be used. If the process of dissolving cladding and fuel is carried out as a single step then a mixed ionic liquid may optionally be used, eg a nitrate and sulfate ionic liquid mixture.

According to a yet further feature of the invention a solvent extraction step may be included to remove uranium and/or plutonium. In one aspect, the solution resulting from the dissolution of the fuel is treated to extract other components of irradiated fuel, after which the uranium and plutonium are separated from the ionic liquid. The uranium and plutonium may be removed together or they may be separated, in which latter case the

ionic liquid liquor is subjected to a uranium/plutonium split operation. The removal of uranium and plutonium may comprise selective dissolution step. Alternatively a fractional crystallisation may be used to bring about the removal of bulk uranium from the other components of irradiated fuel. The selective dissolution may be conducted before or after extraction of other components of irradiated fuel, however it is preferable that a dissolution step is carried out before an extraction step.

The other components of irradiated fuel are suitably removed using a solvent extraction technique, for example one involving the contacting of the ionic liquid solution with a hydrophilic phase, especially an aqueous medium or another ionic liquid into which the other components of irradiated fuel and any Zr are extracted. In another class of embodiments, the ionic liquid solution is contacted with a hydrophobic phase, especially an organic solvent, for example a straight chain hydrocarbon (normally a straight chain alkane) or a mixture of such hydrocarbons, into which the uranium and plutonium are extracted. The solvent extraction technique may involve procedures, such as, for example, oxidation/reduction and/or complexing, to change the solubility properties of one or more selected species in order to control the partition of such species between the two phases.

Thus, some methods include the complexing of one or more dissolved species to change their relative solubilities in the two solvents. In one procedure, TBP (tributyl phosphate) is added to the second phase with which the ionic liquid solution is contacted, in order to complex dissolved uranium and plutonium and thereby effect transfer of those species to the second phase. As an example of the use of oxidation or reduction, it may be mentioned that any uranium/plutonium separation may involve the selective reduction of one of the species into an oxidation state where the reduced or non-reduced species may be selectively extracted into another phase, for example an aqueous or organic phase or another ionic liquid. A reagent for the selective reduction of Pu rather than U is stabilised U(IV) ions. An example of this in Purex reprocessing is the use of U(IV) stabilised by hydrazine.

The invention includes methods in which there is sequential dissolution of different components of the irradiated fuel. In particular, some processes involve a first ionic liquid dissolving the uranium, a second ionic liquid dissolving the plutonium and a third the fission products, not necessarily in this order.

An additional method of bringing about the precipitation of dissolved metals, is via a reduction in temperature of the ionic liquid, in which the uranium is dissolved. A separation process for different metals would be via fractional crystallisation. This particular method further distinguishes the use of ionic liquids from conventional molten salts, since it is impracticable to utilise the method with molten salts as such salts would solidify at lower temperatures.

The uranium, plutonium and fission products may be recovered from the two or three product streams. In those cases in which the product streams have an ionic liquid as solvent, the precipitation of dissolved metals can be induced by changing the acidity and basicity of the ionic liquid by adding or subtracting further ionic components from it. Alternatively precipitation can be brought about by the addition of non-ionic components. For example the precipitation can be brought about by the addition of organic solvents which are miscible or slightly miscible with the ionic liquid. For example in the case of the 1-butyl-3-methyl-imidazolium nitrate, ethyl acetate can be added to bring about the precipitation of a uranium compound. Ethyl acetate is slightly miscible with the ionic liquid, and at the point when the system just becomes biphasic through addition of ethyl acetate, precipitation is optimised.

Volatile non-ionic components added to the ionic liquid can be recovered from the ionic liquid by distillation. The ionic liquid is not volatile. This allows both the organic solvent and the ionic liquid to be recycled to the process.

An alternative means of precipitation is the addition to the ionic liquid of an oxidising or reducing agent.

A preferred process is illustrated by the following flowsheet:

Decladding & dissolution of fuel → Extraction of fission products → Uranium/ plutonium split → Solvent recovery/ destruction

In a second aspect, the ionic liquid liquor containing dissolved fuel and optionally dissolved cladding is subjected to electrochemical treatment to recover the dissolved uranium and plutonium. In one process, the liquor is subjected to electrolysis to deposit the uranium on the cathode as uranium oxide, a uranium compound or uranium metal; the dissolved plutonium may be recovered by a similar route. In some methods, dissolved plutonium is co-deposited on the cathode with the uranium, irrespective of whether the metals are deposited in the metallic state (in the (0) oxidation state), as complexes or as oxides. Such co-deposition is useful in the manufacture of mixed oxide fuels.

Techniques for selecting the ion or ions to be deposited by electrodeposition are well known in the molten salts and metallurgical industries and do not require detailed explanation here. However, it may be noted that all metal ions in a solution will have a different electrode reduction potential which is required to reduce the ion to a lower positive valency, or to reduce it to zero valency. Electrode reduction potentials are unique to the element, to the valency of the ion to the solvent and to the presence of other ions or molecules. If a potential is applied across a solution then all metal ions with a more positive potential will be deposited on the cathode. Metal ions with a more negative potential will remain in solution. Once a particular ion has been removed from the solution, the electrode can be removed and replaced with a new one, run at a slightly more negative potential, for the deposition of the next metal with a more negative reduction potential. If it is the desire to deposit two metals together, then a potential more negative than the reduction potential for both ions is applied to reduce them together.

The cathode material may be selected from known cathode materials, for example. Exemplary materials are carbon, especially glassy carbon, and tungsten.

The ionic liquid is optionally subjected to one or more intermediate steps between dissolution of the fuel and electrodeposition of dissolved species; for example, the ionic

liquid may be treated to reduce the uranium, either by the addition of a reducing agent or by an additional electroreduction step.

After the oxidative dissolution of the uranium oxide together with other soluble components into the ionic liquid, there is a choice of process steps. Amongst these, two are outlined below, although this description is not intended to be limiting.

a) Fractional crystallisation of a uranium compound, and filtration and recovery of this compound. This fractional crystallisation step may be a crude purification of the uranium product. The remaining liquor containing fission products, actinides, lanthanides and plutonium can be subjected to further precipitation, or to electrochemical extraction to separate further uranium and/or plutonium.

b) An electrochemical step can be employed on the bulk of the solution to bring about the separation of uranium and plutonium, from the other components of irradiated fuel.

Optionally, before conducting the electrochemical step the fuel, eg uranium or plutonium, may be purified, for example, by recrystallisation from an ionic liquid.

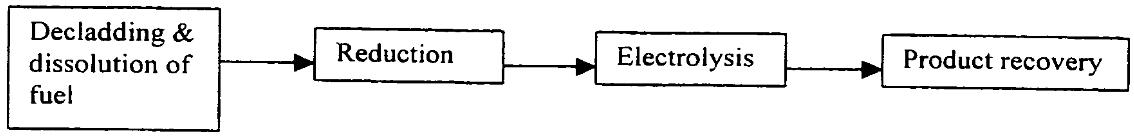
The electrochemical step may require that any excess acid is removed from the system or neutralised. If this is not the case, then any electrodeposited product may be re-oxidised and dissolved by the remaining acid present. Methods of removing the acid include one or more of the following:

(i) ensure that there is an excess of fuel present, to ensure that all acid reacts (excess acid is probably required to drive the process);

(ii) reduce remaining acid (i.e. the proton) electrochemically to hydrogen; and/or

(iii) boil off excess acid, the ionic liquid remaining behind.

A preferred embodiment is illustrated by the following flowsheet:

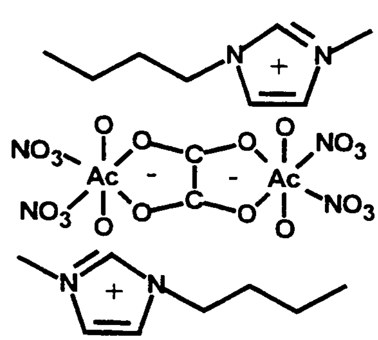


The process illustrated in the flowsheet includes addition of a reductant to the liquor resulting from dissolution and passage of the resultant liquor to an electrochemical apparatus, e.g. an electrochemical bath, where the uranium species is reduced by the application of a current across the electrodes and is deposited at a cathode as uranium metal or another uranium compound. The deposited uranium will be removed from the electrode and passed to a further step for removal of entrapped ionic liquid. A similar process is used to recover dissolved plutonium.

The fuel material produced by the method of the invention is novel per se, in that it has a unique dimeric structure, in which two atoms of fuel material form a dimeric species comprising a dicarboxylate bridge. Although, various dicarboxylates may be used, for example, oxalate, malonate, succinate, glutarate, adipate or pimelate; a preferred bridge moiety is oxalate.

Thus according to a further feature of the invention we provide a fuel material comprising a dimeric species containing two fuel atoms bridged by a dicarboxylate moiety.

In particular we provide a fuel material in which the fuel is uranium. The preferred fuel is uranium. The preferred fuel material has a structure;



in which Ac is Pu or U, preferably U.

Although the structure given in I above is representative, it is understood that bonding of the nitrate groups is via one of the oxygen atoms.

The fuel material of the invention also provides a unique X-ray diffraction pattern. Thus according to the invention we provide a fuel material a molecular structure as shown in Fig. 2 which is derived by X-ray diffraction.

The method of the invention will now be illustrated but in no way limited with reference to the following Examples and the accompanying drawings

Example 1

Preparation of 1-butyl-3-methylimidazolium nitrate ionic liquid

1-Methylimidazole was distilled under vacuum and stored under dinitrogen prior to use. 1-Butyl-3-methylimidazolium or 1-alkylpyridinium salts were prepared by direct reaction of the appropriate alkyl halide with 1-methylimidazole or pyridine, respectively, and recrystallised from ethanenitrile and ethyl ethanoate.

Nitrate ionic liquids were all prepared by methods analogous to the following method used to prepare 1-butyl-3-methylimidazolium nitrate.

1-butyl-3-methylimidazolium chloride (8.04 g, 46.0 m mol) was dissolved in water (15 cm^3). To this solution a solution of silver(I) nitrate (7.82 g, 46.0 m mol) in water (20 cm^3) was added. A white precipitate (silver(I) chloride) formed immediately. The mixture was stirred (20 min) to ensure complete reaction, and was then filtered twice through a P3 sintered glass funnel to remove the white precipitate (the second filtration was generally necessary to remove the final traces of precipitate). The water was removed on a rotary evaporator, yielding a yellow or brown viscous liquid, sometimes

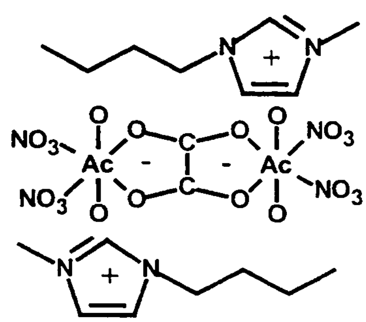
containing small black solid particles. This crude product, 1-butyl-3-methylimidazolium nitrate, was dissolved in a small quantity of dry acetonitrile, and decolourising charcoal was added to the solution. This was then stirred (30 min) and filtered through Celite®. The acetonitrile was removed under vacuum, and the pale yellow ionic liquid product then dried by heating *in vacuo (ca.* 50 °C, 2-3 d). Some discoloration of the product occurred if the heating was too vigorous. Residual silver(I) chloride as removed by electrolysis; silver metal is electroplated at the cathode; and chlorine gas is evolved at the anode. The resulting ionic liquid was stored under dinitrogen to exclude moisture.

Example 2

Results of crystallisation process

The following procedure and results, back up the crystallisation process. In a round bottomed flask, 9.32 g [bmim][NO_3], 4.73 g of conc. aqueous HNO_3, and 4.00 g UO_2 were combined. This mixture was stirred and heated to 70°C for 16 hours. The bright yellow solution which formed, was allowed to cool to room temperature, and to stand overnight. This resulted in the formation of pale yellow crystals. These were removed from the solution by vacuum filtration, using a P4 frit. The vacuum was maintained for up to eight hours, in order to bring about as much removal of the ionic liquid as possible. The crystals formed were then rinsed with cold ethyl acetate to remove any residual ionic liquid. A uranyl salt has been identified analysis of which has identified the molecular as C18H30N8O20U2, and the elemental weight percents are: 18.73% C; 2.62% H; 9.71% N; 27.72 % O; and 41.23 % U.

X-ray diffraction studies have determined the structure as that shown below;



and generally of the structure shown in Figure 2, in which the Cell Parameters are;

A = 15.452

B = 20.354

C = 10.822

β = 106.84

Example 3

Electrochemical Reduction of the Uranyl Salt

0.2655 g (0.23 m mol)of the uranyl salt, precipitated from a uranyl solution in [bmim][NO_3] + HNO_3 by cooling (as explained in Example 2) and recrystallised from acetonitrile, was added to 28.12 g pure [bmim][NO_3] (ca. 25 mL) and dissolved by heating (ca 50°C) and stirring while sparging with dry nitrogen. Complete dissolution occurred within 15 minutes. Nitrogen sparging was continued for one hour.

Electrochemical reduction of the uranyl salt may produce UO_2 which is insoluble in the ionic liquid and should precipitate from solution. Every mole of uranyl salt is believed to produce two moles of UO_2. Therefore, complete reduction of 0.23 m mol of the uranyl salt to UO_2 should yield 0.46 m mol UO_2. Furthermore, since each mole of UO_2 produced

requires two mole equivalents of electrons, the total charge required during the production of 0.46 m mol UO_2 should be 88.8 C.

An electrolysis cell was set up in a three-electrode cell with the uranyl solution as the bulk solution. The reference electrode was a silver wire immersed in a 0.1 mol L^{-1} solution of $AgNO_3$ in [bmim][NO_3] separated from the bulk solution in a glass tube with a porous vycor tip. The counter electrode was a platinum coil immersed in pure [bmim][NO_3] separated from the bulk solution in a glass tube with a glass frit. The working electrode was a flag (ca 3 cm x 2 cm x 0.1 cm) formed from a sheet of glassy carbon.

Electrolysis was carried out on the stirred uranyl solution under a dry nitrogen atmosphere by holding the cathode potential at −1.5 V versus Ag(I)/Ag. During electrochemical reduction of the uranyl salt, the cathode became passivated and electrolysis was halted, perhaps by the adsorption of the UO_2 product. Two techniques were used simultaneously to keep the cathode from becoming passivated. Dry nitrogen was bubbled across the electrode remove passivating material such as adsorbed UO_2. Instead of holding the cathode at −1.5 V constantly, the working electrode potential was periodically stepped to +1.0 V (where it acts as an anode). Typically, the working electrode was held at 1.5 V for 9.6 s and pulsed to +1.0 V for 0.4 s. Used in conjunction, nitrogen sparging and potential pulsing kept the electrode from passivating.

During the electrolysis, the solution lost the bright yellow colour associated with uranyl salts and turned brown. Toward the end of the electrolysis, a dark brown precipitate was noted. After the passage of 95 C, electrolysis was halted as the current dropped dramatically. Voltammograms recorded at a glassy carbon disk working electrode before and after electrolysis (Figure 1) demonstrate the elimination of uranyl from the solution. Scans of the electrode potential were initiated at 0 V, scanned to the cathodic limit of the ionic liquid, reversed and scanned to anodic limit, and then returned to 0 V.

Series 1 (blue) shows a voltammogram recorded in the neat solution. The electrochemical window of the ionic liquids is demonstrated as stretching from ca. −2.2V, where the organic cation is reduced, to ca. +1.5V, where nitrate is oxidised.

Series 2 (violet) shows a voltammogram recorded in the 0.1 mol L^{-1} uranyl solution prior to electrolysis. The wave with a peak around –0.9 V represents the reduction of uranyl. A much smaller anodic wave can be seen around 0 V. Lack of an anodic wave of equal size during the reverse scan indicates that the reduction is chemically irreversible. The broadness of the cathodic wave indicates slow electron transfer.

Series 3 (yellow) shows a voltammogram recorded in the bulk solution after electrolysis. There is very little current above the background current of the ionic liquid (blue). A slight rise in current around —.2 V indicates that the electrolysis was not 100% complete.

The solution was diluted with acetone (to make the solution less viscous) and the precipitate was collected by vacuum filtration through size P4 glass frit.

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CLAIMS

1. A method for treating or reprocessing spent nuclear fuel to substantially separate fissile material from other components of irradiated fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid.

2. A method according to Claim 1 which includes a separate step of solvent extraction to remove uranium.

3. A method according to Claim 1 which includes a separate step of solvent extraction to remove plutonium.

4. A method according to Claim 1 which includes a separate step of solvent extraction to remove uranium and plutonium together.

5. A method of Claim 1 in which the liquor is contacted with a hydrophilic solvent into which the fission products are extracted.

6. A method of Claim 5 in which the hydrophilic solvent comprises an aqueous medium or an ionic liquid.

7. A method of Claim 1 in which the liquor is contacted with a hydrophobic solvent into which the fission products are extracted.

8. A method of Claims 2 to 4 in which the liquor is contacted with a hydrophobic solvent into which the fissile material is extracted.

9. A method of Claim 8 wherein the fissile material is precipitated by adjusting the pH of the solvent into which the fissile material is extracted.

10. A method of Claim 8 wherein the fissile material is precipitated by adding a non-ionic component to the solvent into which the fissile material is extracted.

11. A method of Claim 8 wherein the fissile material is precipitated by fractional crystallisation.

12. A method of Claim 8 in which the hydrophobic solvent comprises one or more straight chain hydrocarbons.

13. A method of Claim 1 in which the solvent extraction involves controlling the solubility properties of one or more species by complexing, oxidising or reducing the species.

14. A method of Claim 1 wherein the nuclear fuel comprises a cladding and the method includes dissolution of the cladding in the ionic liquid.

15. A method of Claim 14 in which the cladding is zirconium alloy cladding.

16. A method of any of Claims 1 to 13 wherein the nuclear fuel comprises a cladding and the method comprises removal or rupturing of the cladding before dissolution of the fuel.

17. A method of Claim 1 in which the ionic liquid contains an agent to enhance the oxidising ability of the ionic liquid, to enable it to oxidise U(IV) to U(VI) and possibly Pu(IV) to Pu(VI).

18. A method of Claim 17 in which the ionic liquid contains both nitrate anions and a Brønsted or superacid.

19. A method of Claim 18 in which the acid is a Brønsted acid or Franklin acid.

20. A method of Claim 19 in which the acid is HNO_3, H_2SO_4 or $[NO]^+$, e.g. from $[NO][BF_4]$.

21. A method according to Claim 20 in which the $[NO]^+$ is from $[NO][BF_4]$.

22. A method of Claim 1 in which the ionic liquid is based on a 1,3-dialkyl imidazolium nitrate and wherein the alkyl groups may be the same or different.

23. A method of Claim 1 in which the ionic liquid is based on a sulfate.

24. A method according to Claim 23 wherein the ionic liquid is based on $[bmim]_2[SO_4]$.

25. A method according to claim 23 wherein the ionic liquid is based on $[bmim][HSO_4]$.

26. A method of Claim 1 which is a method for reprocessing nuclear fuel to form a fissile material optionally in the form of a gel, a powder, a master batch material, a fuel pellet, a fuel pin or a fuel assembly.

27. A method for treating or reprocessing spent nuclear fuel to separate or partially separate fissile material from fission products, in which method the fuel is dissolved in an ionic liquid and the resultant liquor is subjected to electrolysis to deposit dissolved uranium compound at the cathode.

28. A method of Claim 27 wherein the nuclear fuel comprises zirconium alloy cladding and the method includes dissolution of the cladding in the ionic liquid.

29. A method of Claim 27 wherein the nuclear fuel comprises a cladding and the method comprises removal or rupturing of the cladding before dissolution of the fuel.

30. A method of any of Claims 27 to 29 in which the ionic liquid is subjected to one or more intermediate steps between dissolution of the fuel and electrodeposition of dissolved uranium.

31. A method of Claim 30 in which the intermediate steps comprise treatment of the ionic liquid to reduce dissolved uranium.

32. A method of any of Claims 27 to 31 which further comprises subjecting the liquor, before or after electrodeposition of dissolved uranium, to electrolysis to deposit dissolved plutonium or a plutonium compound at the cathode.

33. A method of any of Claims 27 to 31 in which dissolved plutonium is co-deposited on the cathode with the uranium.

34. A method of any of Claims 27 to 31 which is a method for reprocessing nuclear fuel to form a fissile material optionally in the form of a gel, a powder, a master batch material, a fuel pellet, a fuel pin or a fuel assembly.

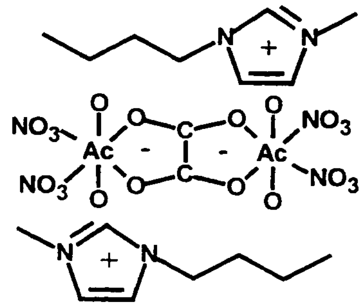
35. A fuel material comprising a dimeric species containing two fuel atoms bridged by a dicarboxylate moiety.

36. A fuel material according to Claim 35 wherein the fuel atoms are either both U or both Pu.

37. A fuel material according to Claim 36 wherein the fuel atoms are both U.

38. A fuel material according to Claim 35 wherein the dicarboxylate moiety is oxalate.

39. A fuel material according to Claim 36 having a structure



wherein Ac is Pu or U.

40. A fuel material according to Claim 39 wherein Ac is U.

41. A fuel material according to Claim 35 which has a molecular structure substantially as defined by Figure 2.

42. A method for treating or reprocessing spent nuclear fuel substantially as herein before described with reference to the accompanying description and drawing.

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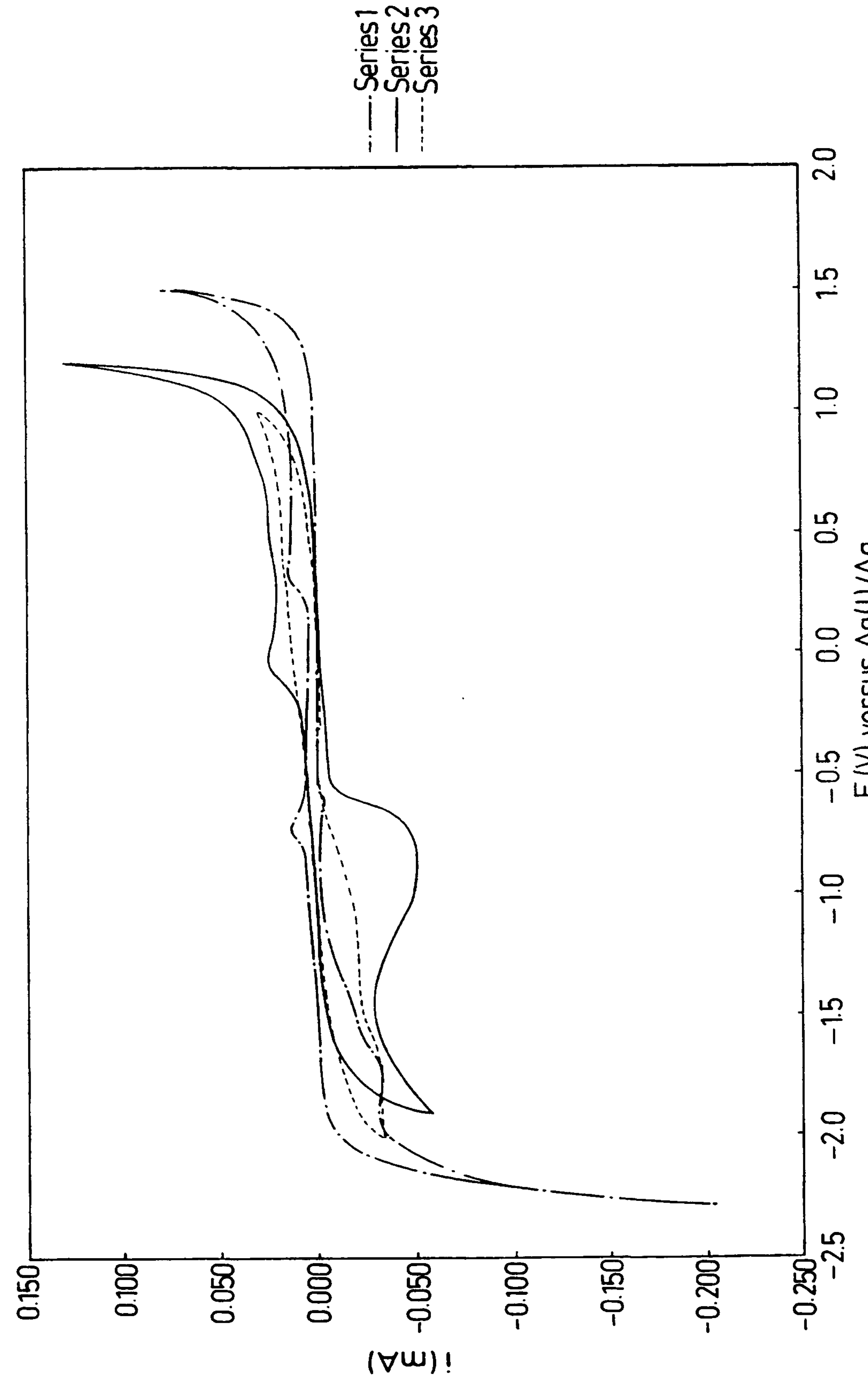

Fig. 1

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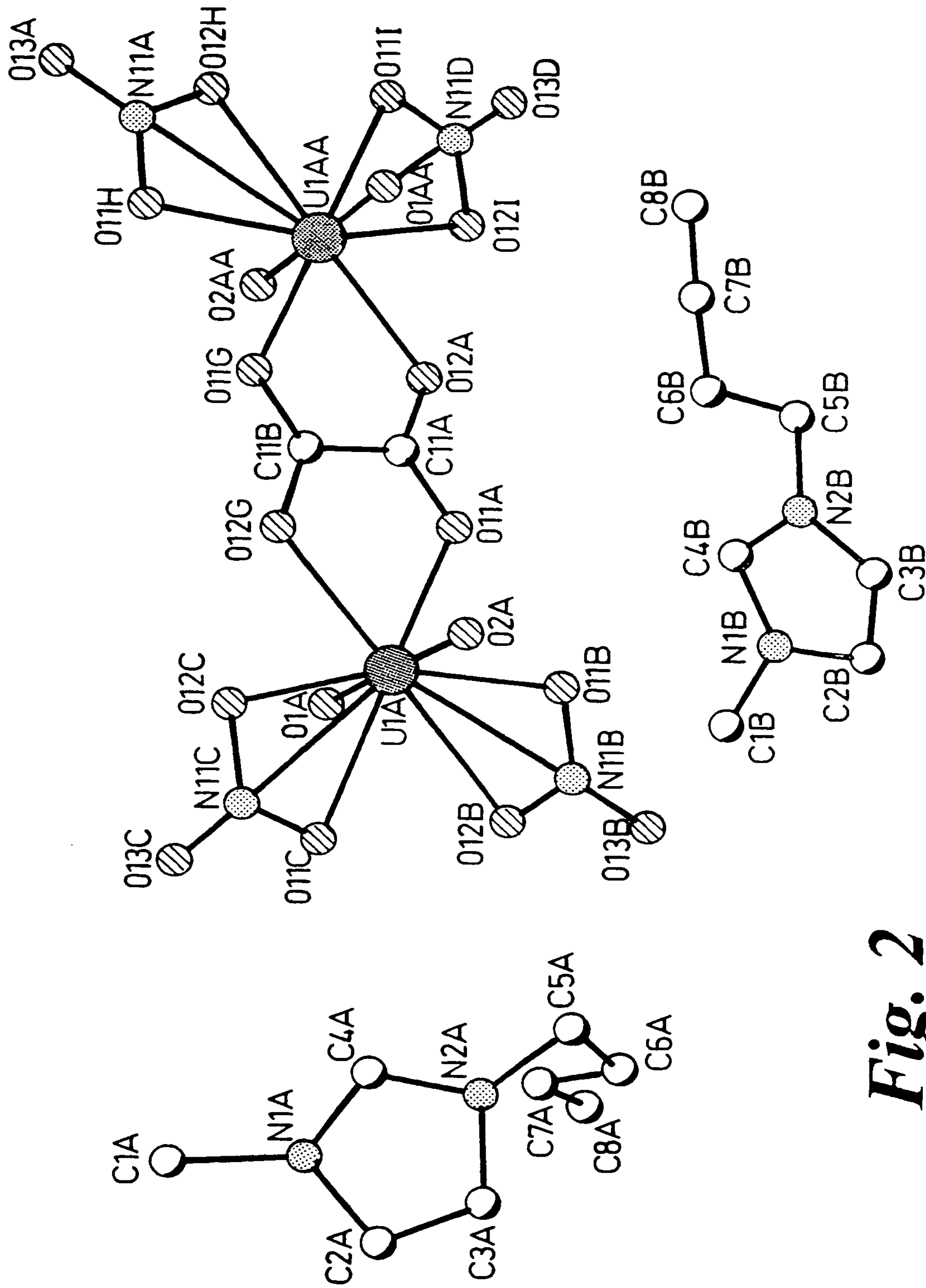
013A
N11A
012H
011I
N11D
013D
U1AA
011H
01AA
012I
02AA
011G
012A
C11B
C11A
012G
011A
02A
012C
01A
U1A
011B
N11C
N11B
013C
011C
012B
013B
C8B
C7B
C6B
C5B
N2B
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C3B
N1B
C2B
C1B
C1A
N1A
C4A
N2A
C5A
C6A
C7A
C8A
C2A
C3A

Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/00246

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G21C19/48 G21C3/58 C07F5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G21C C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	LEGROS, JEAN P. ET AL: "Structure of the.mu.-oxalatobis' dioxalatodioxouranium (VI)! ion '(UO2)2(C2O4)5!6-" ACTA CRYSTALLOGR., SECT. B (1976), B32(8), 2497-503 CODEN: ACBCAR,1976, XP002106906 see page 2500 --- -/--	35-38

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 June 1999	06/07/1999

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International Application No
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